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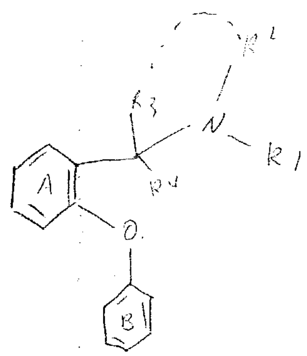

A, B can also be naphthenyl

R^2, R^3 can be independent. They may also form a ring.

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  - ☐ Helped examiner better understand the invention.
  - ☐ Helped examiner better understand the state of the art in their technology.

  Types of relevant prior art found:
  - ☐ Foreign Patent(s)
  - ☐ Non-Patent Literature
    (journal articles, conference proceedings, new product announcements etc.)
- *Relevant prior art **not found:***
  - ☐ Results verified the lack of relevant prior art (helped determine patentability).
  - ☐ Results were not useful in determining patentability or understanding the invention.

Comments:

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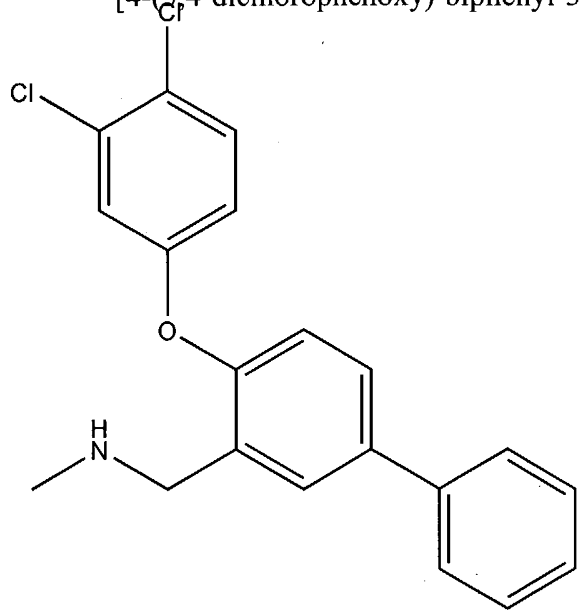
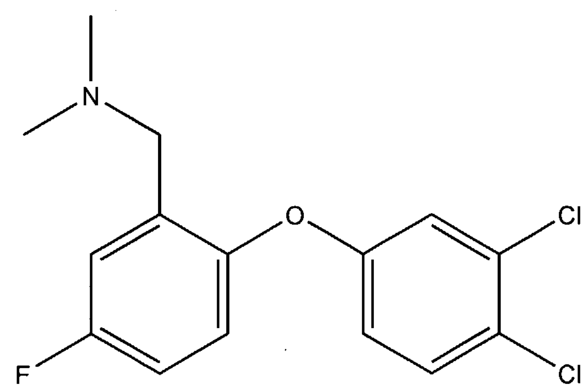
sira

[4-(3,4-dichlorophenoxy)-biphenyl-3-ylmethyl]-methylamine



[2-(3,4-dichlorophenoxy)-5-fluorobenzyl]-dimethylamine



Epicupreine. L. Prajer and J. Suszko (Poznań Univ.). *Bull. soc. amis sci. et lettres Poznań Ser. B* **13**, 53–66, 67–77, 79–89(1956)(in English).—See *C.A.* 49, 2448*f*.
H. M. Leicester

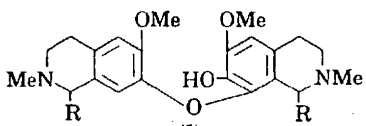
Chelates and conformation of cinchona bases. Zoltán Földi, Tamás Földi, and András Földi (Authors' Lab., Budapest). *Chem. & Ind.* (London) **1957**, 465–6.—Epiquinidine (648 mg.) ground with 5 ml. 0.2*M* $CuSO_4$ gives an addn. compd. which with *N* NaOH yields microcrystals of the chelate $(C_{20}H_{23}O_2N_2)_2Cu$. The chelate of epiquinine is similarly obtained. Both chelates decomp. 150–90° and show no characteristic m.p. All attempts to prepare chelates from quinine, quinidine, cinchonine, and cinchonidine failed. The readiness to form a chelate suggests that in the epi-bases the alc. H is chelated by O and N, giving rise to a 5-membered ring and to an addnl. asymmetry absent in the C-9 epimers.
Blanche B. White

Asymmetric induction and absolute configuration in the biphenyl series. Jerome A. Berson and Michael A. Greenbaum (Univ. of S. California, Los Angeles). *J. Am. Chem. Soc.* 79, 2340(1957); cf. *C.A.* 51, 1108*i*.—MeMgI converted the phenylglyoxylates of phenyldihydrothebaine (I) and its derivs., 2,5,6-R′(MeO)(HO)$C_6H_2C_6H_3$(OMe)R-3,6 (II) (IIa, R = CH:CH_2; R¹ = $CH_2CHPhNMe_2$) (IIb, R = Et; R¹ = $CH_2CHPhNMe_2$) (IIc, R = CH:CH_2; R¹ = CH:CHPh) to atrolactic esters. Sapon. and isolation without optical fractionation gave (−)-atrolactic acid (III) (abs. configuration shown) in optical yields of 70% from I and 91, 89, and 93% from IIa, IIb, and IIc, resp. Mechanisms for the formation of III are discussed.
Felix Saunders

The structure of pseudomorphine. K. W. Bentley and S. F. Dyke (Univ. Aberdeen, Scot.). *Chem. & Ind.* (London) **1957**, 398.—Pseudomorphine was shown to be 2,2′-dimorphine (cf. Small and Turnball, *C.A.* **31**, 6663⁶, and Goto and Kitasato, *C.A.* 24, 4299). Oxidation of 1-bromodihydromorphine with alk. $K_3Fe(CN)_6$ at 70–80° gave a poor yield of dibromotetrahydropseudomorphine (I), m. above 350°, $[\alpha]^{18}_D$ −46° ± 10° (0.518%, *N* HCl). I was prepd. by bromination of tetrahydropseudomorphine in HOAc.
R. H. Loeppert

Synthesis in the morphinan group. II. The structure of 3-hydroxy-*N*-methyl-*C*-normorphinan. Seiichi Saito (Univ. Tokyo). *Pharm. Bull.* (Tokyo) 4, 438–43(1956); cf. *C.A.* 51, 8117*d*.—As conclusive evidence of the structure of the previously synthesized (*loc. cit.*) title compd. (I) it was submitted to the Hofmann degradation and its degradation products were synthesized. Excess CH_2N_2 in ether added to 2.5 g. I suspended in 25 cc. MeOH, the mixt. kept 5 days at room temp., the solvents evapd., and the residue distd. *in vacuo* yielded 2.3 g. *O*-Me deriv. (II) of I, $b_{0.15}$ 152–3°; picrate, m. 167–9° (from AcOH). Refluxing 40 min. 2.8 g. MeI salt of II with 30 cc. 16% KOH, dissolving the sepd. oil in C_6H_6, and distg. the residue from the C_6H_6 soln. *in vacuo* yielded 1.6 g. 9b-($Me_2NCH_2CH_2$) deriv. (III) of 8-methoxy-2,3,3a,9b-tetrahydro-1*H*-benz[*e*]indene (IV), $b_{0.06}$ 160° (bath temp.); HCl salt, m. 181–3° (from MeOH-ether). The MeI salt of III (1.4 g.) in 30 cc. warm H_2O shaken 4 hrs. at room temp. with fresh Ag_2O (from 2.4 g. $AgNO_3$ and 10 cc. 3*N* NaOH), the filtrate evapd. to dryness below 50°, and the residue heated *in vacuo* (2–3 mm.) evolved NMe_3 at 90° and distd. 0.6 g. liquid at 90–140°, which, dissolved in ether, washed with 10% HCl, dried, the ether removed, and the residue distd. *in vacuo* yielded 0.5 g. 9b-(CH_2:CH) deriv. (V) of IV, $b_{1.5}$ 130° (bath temp.). V (0.3 g.) in 20 cc. EtOH catalytically reduced (10% Pd-C) absorbed 2 molar equivs. H in 3 hrs. and yielded 0.3 g. 8-methoxy-9b-ethyl-2,3,3a,4,5,-9b-hexahydro-1*H*-benz[*e*]indene (VI), b_1 100–20° (bath temp.); penta-Br deriv. (VII), m. 168–70°(decompn.); λ^{CCl_4} 288 and 298 mμ. Synthesis of VI confirmed its structure and thus indirectly the structure of I. 2-Ethoxycarbonylcyclopentanone (VIII) (23.5 g.) added slowly to 5.6 g. K suspended in 220 cc. abs. PhMe, stirred 1 hr. at room temp., 23.5 g. *p*-$MeOC_6H_4CH_2CH_2Br$ added dropwise, the mixt. refluxed 10 hrs., cooled, and H_2O added yielded from the org. layer 20 g. 2-(*p*-$MeOC_6H_4CH_2CH_2$) deriv. of VIII, $b_{1.5}$ 168–70°, which refluxed 3 hrs. with 95 cc. AcOH, 45 cc. concd. HCl, and 150 cc. H_2O, the mixt. concd. to 0.25 vol. *in vacuo*, and extd. with C_6H_6 was converted to 12 g. 2-(*p*-methoxyphenethyl)cyclopentanone (IX), $b_{1.5}$ 130–7°; semicarbazone, m. 205–7° (decompn.). IX (12 g.) in 50 cc. PhMe added to the Grignard reagent from 26.4 g. EtBr, 6 g. Mg, and 30 cc. abs. ether, distd. to 85°, refluxed 5 hrs., decompd. with ice H_2O contg. HCl, and worked up as usual yielded 11 g. 1-ethyl-2-(*p*-methoxyphenethyl)cyclopentene, b_2 138–43°, which, added to 35 cc. 85% H_2SO_4 at 0–5°, stirred 30 min. at 15–20°, and extd. with C_6H_6, was cyclized to 8.5 g. VI, $b_{1.5}$ 116–18°; penta-Br deriv. (X), m. 168–70° (decompn.), undepressed by VII. The ultraviolet and infrared spectra of both VI obtained by degradation and by synthesis agreed well (curves shown). Detn. of the positions of Br in X was attempted. VI (0.5 g.) in 20 cc. $CHCl_3$ kept at room temp. 1 hr. with 0.4 cc. Br, refluxed 30 min., $CHCl_3$ evapd., the residue heated 10 min. on a steam bath with 15 cc. AcOH and 0.01 cc. Br yielded 9% tetra-Br deriv. (XI) of VI, m. 172–4° (decompn.), λ^{CCl_4} 287 mμ (log ε 3.74). X (0.7 g.) refluxed 5 hrs. with 0.7 g. $MgCO_3$, 15 cc. dioxane, and 15 cc. H_2O, poured into 30 cc. H_2O, and extd. with C_6H_6 yielded 0.35 g. (probably) 5-hydroxy deriv. (XII) of XI, m. 168–70°, λ^{EtOH} 282 and 291 mμ (log ε 3.46 and 3.53), and this by oxidation with CrO_3 yielded 65% 5-oxo deriv. (XIII) of XI, m. 186–8°, λ^{EtOH} 245 and 287 mμ (log ε 4.11 and 3.89). These results, together with the infrared spectra of X-XIII, led to the tentative conclusion that X is the 4,5,6,7,9-Br_5 deriv. of VI.
H. S. French

Alkaloid studies. XVII. The structure of the cactus alkaloid pilocereine. Carl Djerassi, S. K. Figdor, J. M. Bobbitt, and F. X. Markley (Wayne State Univ., Detroit, Mich.). *J. Am. Chem. Soc.* **79**, 2203–10(1957); cf. *C.A.* **51**, 8118*d*.—Structure I (R = CH_2CHMe_2) was elucidated for the cactus alkaloid *pilocereine*. I (8.5 g.) in 200 cc.



(I)

MeOH-280 cc. Et_2O treated 6 days at 0° with 2.2 g. distd. CH_2N_2, the mixt. treated with an addnl. 2.2 g. CH_2N_2, kept 3 days at 0°, and evapd. and the residue recrystd. from hexane yielded 6.5 g. *Me ether* (II) of I, m. 92–105°, resolidified and m. 153–5° (all m.ps. were detd. on a Köfler block). II, m. 153–5° (from EtOAc), was transformed to a 2nd cryst. form, m. 133–5°; the transformation was reversed by recrystn. from hexane. I (3.0 g.) in 100 cc. abs. EtOH treated with 3.6 g. $MeCHN_2$ in 150 cc. Et_2O, kept 24 hrs. at room temp., treated with an addnl. 3.6 g. $MeCHN_2$, refrigerated 6 days, and evapd. yielded 2.07 g. *Et ether* (III) of I, m. 90–5° and 152–3° (from hexane); 2nd crop, 0.32 g. Amberlite IRA-400 (HCl) (200 g.) treated with 500 cc. 50% aq. NaOH, 2 l. H_2O, and finally 250 g. $NaHCO_3$ in satd. aq. soln. and washed with 12–16 l. H_2O gave the bicarbonate salt IRA-400-HCO_3 which was stored under distd. H_2O. Styphnates and picrates in EtOH or Me_2CO contg. about 5% H_2O passed dropwise over a column of IRA-400-HCO_3, the column washed with 2 vols. 10% aq. Me_2CO, the Me_2CO removed *in vacuo*, acid added, the aq. soln. washed with Et_2O and basified with NH_4OH, and the base isolated with Et_2O gave the corresponding free amines. II (2.5 g.) in 100 cc. 10% H_2SO_4 made just alk. with 2*N* NaOH, treated dropwise at room temp. with 250 cc. 2% aq. $KMnO_4$, allowed to stand overnight, acidified with H_2SO_4, and extd. continuously with Et_2O, the residue from the ext. treated with $SOCl_2$ and then $PhNH_2$, and the product chromatographed yielded 35 mg. iso-PrCONHPh and 10 mg. iso-BuCONHPh. I (5.0 g.) in 200 cc. dry Et_2O added slowly with stirring to 1.5 l. liquid NH_3 at −60° during 5 hrs., the mixt. warmed during 3 hrs. to −30°, treated cautiously with NH_4Cl and evapd. overnight, the residue partitioned between Et_2O and 3% aq. NaOH, the alk. layer acidified with 40% H_2SO_4, washed with Et_2O, basified with concd. NH_4OH, and extd. with Et_2O, and the ext. evapd. gave 2.46 g. phenolic basic oil (IV); the original Et_2O layer extd. with 10% HCl, dried, and evapd. left only a small amt. of nonphenolic, nonbasic oil which was discarded; the acid ext. basified with NH_4OH and extd. with Et_2O gave 2.40 g. nonphenolic, basic, glassy material (V). V consisted mainly of *isopilocereine* (VI); *dipicrate*, m. 235–7° (from Me_2CO). VI dipicrate (3.5 g.) treated with LiOH and the resulting free base treated with CH_2N_2 in Et_2O-MeOH yielded 55% *Me ether* (VII) of VI, $b_{0.005}$ 180–90° (evaporatively distd.). In 1 run, a 75-mg. aliquot of V treated with 40 mg. picric acid yielded 70 mg. *1-isobutyl-2-methyl-6-methoxy-1,2,3,4-tetrahydroisoquinoline* (VIII) *picrate*, m. 150–1° (from MeOH). IV (0.26 g.) treated 6 days at 0° with CH_2N_2 in Et_2O contg. a small amt.

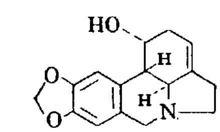
of MeOH and evapd., the residue extd. with Et_2O and washed with 3% aq. NaOH, and the resulting oil (0.2 g.) chromatographed on 9 g. Al_2O_3 gave 0.155 g. *7-MeO deriv.* (IX) of VIII, n_D^{25} 1.5284; *styphnate*, m. 212–13°; *picrate*, m. 184–5°. I (5 g.) in 1.5 l. dry NH_3 treated at −30° with 6 g. K, and the mixt. worked up in the usual manner gave 1.79 g. V and 2.68 g. IV; the IV dissolved in Et_2O, dried, and concd. yielded 1.45 g. *demethylisopilocereine* (X), m. 177.5–78°. X (100 mg.) treated 2 days at 0° with excess CH_2N_2 in Et_2O and evaporatively distd. yielded 81 mg. glass, the infrared spectrum of which closely resembled that of VI; treatment with picric acid gave a small amt. of VI picrate. X (210 mg.) in Et_2O-MeOH treated 7 days with CH_2N_2 yielded 120 mg. VII. IV (300 mg.) treated 7 days at room temp. with 0.84 g. $MeCHN_2$ in Et_2O, washed with alkali, and treated with picric acid gave the *picrate* of the *7-EtO deriv.* of VIII, m. 151.5–2.5°. Natural IX (2.2 g.) oxidized with $KMnO_4$ yielded 310 mg. *m*-hemipinic acid, characterized as the di-Me ester, m. 89.5–90°; iso-$PrCO_2H$ and iso-Bu-CO_2H were identified as their anilides. IX (2.47 g.) and 10 cc. MeI kept overnight at room temp., the resulting methiodide (5.17 g.) dissolved in a small amt. of H_2O, added to 120 cc. 50% aq. KOH, and refluxed 2 hrs., and the product isolated in the usual manner yielded 2.05 g. *2,4,5-[iso-Bu(Me_2N)CH]($MeO)_2C_6H_2CH:CH_2$* (XI), oil. XI (185 mg.) in glacial AcOH ozonized 0.5 hr. at 15° and steam distd. into dimedon in MeOH, and the mixt. kept 24 hrs. at 0° gave 39 mg. CH_2O deriv., m. 193–5°. XI (1.87 g.) in MeOH hydrogenated 1 hr. over 5% Pd-C yielded the *1-Et analog* (XII) of XI. XII converted to the methiodide (3.94 g.) and boiled with 50% aq. KOH yielded 1.06 g. neutral N-free oil, apparently 3,4,5-Et$(MeO)_2C_6H_2CH:CHCHMe_2$; a 90-mg. portion ozonized and steam distd. into acidified aq. 2,4-$(O_2N)_2C_6H_3NHNH_2$, extd. with C_6H_6, and chromatographed on Al_2O_3 yielded 20 mg. iso-PrCHO deriv., m. 181–2°. IX oxidized with $KMnO_4$ in the same manner as I gave iso-$PrCO_2H$ and iso-$BuCO_2H$. VII (104 mg.) in C_6H_6 treated 4.5 hrs. with 1 cc. MeI gave 153 mg. *VII.2MeI*, m. 191–4° (from hexane-Me_2CO). VII.2MeI (150 mg.) in 5 cc. MeOH and 20 cc. H_2O passed 4 times over IRA-400-OH resin, the column washed with 20 cc. 50% aq. MeOH, and the residue from the eluates distd. yielded 89 mg. gummy methine, $C_{33}H_{50}N_2O_4$, $b_{0.005}$ 170–5°; a 100-mg. sample ozonized in $CHCl_3$ at −60° gave 55 mg. CH_2O-dimedon deriv.; a 500-mg. sample in EtOH hydrogenated 10 min. over Pd-C yielded 450 mg. reduced methine (XIII), $b_{0.005}$ 160° (bath temp.). XIII (130 mg.) in Et_2O treated with MeI, the dimethiodide (180 mg.) decompd. by the ion exchange resin method, the resulting neutral olefin (76 mg.), $b_{0.005}$ 160–80°, ozonized in $CHCl_3$ at −60°, and the distillate passed into 2,4-$(O_2N)_2C_6H_3NHNH_2$ soln. yielded 44% 2,4-$(O_2N)_2$-$C_6H_3NHN:CHCHMe_2$ (XIIIa). II (2.56 g.) treated with MeI, the II.MeI (3.9 g.), m. 137–50° (decompn.), powd., added to 100 cc. refluxing 40% aq. NaOH, and refluxed 2.5 hrs., a 160-mg. portion of the resulting *methine* 4,2,-5-R(MeO)[CH(NMe_2)(CH_2CHMe_2)]$C_6H_2OC_6H(OMe)_2$[CH-(NMe_2)(CH_2CHMe_2)]R-2,3,6,5 (XIV) (*R = CH:CH₂*) (2.0 g.) ozonized in AcOH, and the mixt. steam distd. into 2,4-$(O_2N)_2C_6H_3NHNH_2$ gave only 47 mg. CH_2O deriv. XIV (R = $CH:CH_2$) (1.9 g.) in 50 cc. 95% EtOH hydrogenated over 300 mg. 10% Pd-C, and the crude product (1.85 g.) recrystd. from MeCN gave 0.92 g. XIV (*R = Et*), m. 101.5–3.5°. XIV (*R = Et*) (1.21 g.) subjected to a 2nd stage Hofmann degradation gave 0.45 g. Me_3N picrate, m. 206–10°, and 0.84 g. N-free degradation product which ozonized in EtOAc at −60° and worked up in the usual manner yielded only 3% XIIIa. XIV (R = Et) converted to the dimethiodide (1.72 g.) and subjected to a Hofmann degradation in the usual manner except that the compd. was first dissolved in EtOH gave a substance, $b_{0.005}$ 155–70°, which appeared to be the *di-CH(OEt)CH₂CH-Me₂ analog* (XV) of XIV (R = Et). II (1.98 g.) cleaved in the usual manner with 90 cc. Et_2O, 600 cc. liquid NH_3, and 2.5 g. *K* at −60° during 7 hrs. gave 1.30 g. nonphenolic basic and 0.67 g. phenolic basic fractions. The nonphenolic fractions dissolved in 20 cc. hexane and chromatographed on 80 g. Al_2O_3 (deactivated with 2.4 cc. 10% AcOH), giving 114 fractions, and fractions 20–46 (hexane up to 1:1 hexane-C_6H_6) treated with alc. picric acid gave 0.53 g. picrate of VIII, m. 152–3°; fractions 47–83 (1:1 hexane-C_6H_6 to 99:1 C_6H_6-Et_2O) treated with alc. picric acid gave 0.196 g. IX picrate, m. 183–5°. Fractions 100–12 (9:1 C_6H_6-Et_2O) gave similarly 10% *picrate* of the *8-OH deriv.* (XVI) of IX, m. 150–5°. XVI (73 mg.) (from the picrate) treated 10 days at 0° with CH_2N_2 in Et_2O-MeOH and the product treated with alc. picric acid yielded the *picrate* of the *8-MeO analog* (XVII) of XVI, m. 132–4°. Fractions 112–14 (Et_2O and 9:1 Et_2O-MeOH) gave a picrate, m. unsharply above 210°, which may represent dimeric material. The phenolic cleavage product (0.67 g.) and CH_2N_2 in MeOH-Et_2O refrigerated 8 days yielded 0.43 g. picrate of IX, m. 181–4°; the mother liquors transformed to the free amine by the ion exchange method and chromatographed on deactivated Al_2O_3 gave 0.164 g. oil which treated with picric acid yielded 0.175 g. picrate of XVII. III (2.04 g.) in 80 cc. Et_2O and 600 cc. liquid NH_3 treated at −60° with 3.3 g. K and the mixt. worked up after 24 hrs. gave 1.30 g. nonphenolic basic and 0.51 g. phenolic basic fractions. The nonphenolic portion chromatographed in the usual manner gave 0.576 g. VIII picrate, m. 151–3°, 0.227 g. *picrate* of the *7-EtO analog* (XVIII) of IX, m. 152–3°, and 0.244 g. *picrate* of the *8-OH deriv.* of XVIII, m. 153–4°. The phenolic portion (0.51 g.) methylated in the usual manner and treated with picric acid gave 0.356 g. picrate of IX, m. 183–5°.

F. W. Hoffmann

Veratrum alkaloids. IV. Analysis of veratrine by paper chromatography. Karel Macek, Stanislav Vaněček, Vendulka Pelcová, and Zdeněk J. Vejdělek. *Collection Czech. Chem. Communs.* 21, 1182–7(1956)(in German).—See *C.A.* 59, 10115*i*.

E. J. C.

Alkaloids of the amaryllidaceae. X. The structure of caranine. E. W. Warnhoff and W. C. Wildman (Natl. Insts. of Health, Bethesda, Md.). *J. Am. Chem. Soc.* 79, 2192–8(1957); cf. *C.A.* 50, 16803*h*; 51, 3624*d*.—A combination of degradative expts. substantiated structure



(I)

I for the alkaloid *caranine*. I was recovered unchanged after 2 hrs. reflux in 10% HCl, 1 hr. reflux in 10% alc. NaOH, and 4 hrs. reflux in 90% HCO_2H. The pK_a values were detd. in 3:7 $HCONMe_2$-H_2O for the following compds.: I 7.60, *α-dihydrocaranine* (II) 9.00, lycorine 6.90, and dihydrolycorine 8.67. I (150 mg.) in 10 cc. dry tetrahydrofuran refluxed 25 hrs. with 150 mg. $LiAlH_4$ gave 138 mg. oily product which crystd. from EtOAc gave 111 mg. unchanged I, m. 178.5–81° (all m.ps. are cor.). I (200 mg.) stirred 2 hrs. with 1.00 g. MnO_2 in 10 cc. $CHCl_3$, filtered, and evapd., and the residual brown glass (146 mg.) sublimed at 145° and 2 μ gave 106 mg. crude I and 40 mg. unsublimed brown residue, insol. in org. solvents and dil. HCl. I (1.00 g.) in 50 cc. H_2O contg. 6 cc. 10% HCl made just basic with 10% aq. NaOH, treated with stirring with 5.00 g. $KMnO_4$ in 250 cc. H_2O dropwise during 45 min., stirred 15 min., treated with SO_2 and then a few cc. dil. H_2SO_4, and extd. with EtOAc, the yellow solid residue (413 mg.) from the ext. triturated with 10% aq. $KHCO_3$ and filtered, the filtrate acidified and extd. with EtOAc, the solid residue (178 mg.) from the ext. refluxed 3.5 hrs. with 8 cc. 20% aq. NaOH under N, the mixt. acidified and extd. with EtOAc, and the residual gum (84 mg.) sublimed at 160° and 0.3 mm. gave 12.5 mg. crude *hydrastic anhydride* (III), m. 168–75°; the original aq. layer from the oxidation extd. continuously with Et_2O and the resulting brown oil (83 mg.) sublimed at 160° and 0.3 mm. gave 8.5 mg. crude III, m. 140–55°. Sublimed III (4.5 mg.) recrystd. from cyclohexane-Me_2CO yielded 3.0 mg. pure III, m. 179–80.5°. Crude III (8.0 mg.) triturated with 2 drops 30% aq. $EtNH_2$ and evapd., and the residue sublimed at 160° and 0.3 mm. gave 8.0 mg. *N-ethylhydrastimide*, m. 168.5–9.5° (from EtOH). I (5.000 g.) in 30 cc. glacial AcOH and 400 mg. prereduced PtO_2 in 5 cc. glacial AcOH hydrogenated 2 hrs., filtered, and evapd., the residue basified with 10% aq. KOH and extd. with EtOAc, and the ext. evapd. yielded 3.626 g. II, m. 170.5–72° (from EtOAc), $[\alpha]_D^{26}$ −126° (*c* 0.441) (all rotations were taken in $CHCl_3$); *picrate*, clusters of yellow needles, m. 149–50° and 172–3° (decompn.) (from Me_2CO-EtOH). II was identical with *monodeoxydihydrolycorine* (cf. Takeda and Kotera, *C.A.* 50, 16802*a*). I (300 mg.) in 9 cc. EtOH hydrogenated at ambient conditions over 100 mg. 10% Pd-C, filtered, and evapd., and the

but with morpholine, XVII, XVIII, XLI, XLII, XXIX, XXX, XXXI, XXVIII, LIII, and LIV gave 75% LXV, LXVI, 75% LXVII, LXVIII, LXII, LXIII, 80% LXIV, LXI, 80% LXIX, and LXX, resp. XI (25 g.) refluxed 15 hrs. at 50° with 16.5 g. glacial HOAc and 17 g. chloromethyl ether, H_2O added, the mixt. extd. with Et_2O, the Et_2O layer washed, dried, and distd. gave 50% mixt. (CI), $b_{0.5}$ 140–50°, of LI and LII. CI treated with XCIX gave a mixt. of HCl salts of LIII and LIV, from which LIV, but not LIII, could be recovered by crystn. from abs. EtOH. The HCl salts of XLVI, LX, LVIII, and LV were hygroscopic and difficult to recrystallize. J. March

1-Oxa-7,8-benzodidehydroindolizidine from 3,4-dihydroisoquinoline and study of 1-methyl-3,4,5,6,7,8-hexahydroisoquinoline. Woldemar Schneider and Bertold Müller (Tech. Hochschule, Karlsruhe, Ger.). *Arch. Pharm.* 294, 360–5(1961).—3,4-Dihydroisoquinoline (I) (5 g.) in 20 ml. C_6H_6 was treated with 4.8 g. $BrCH_2CH_2OH$ 6 days at room temp. to give 92% 2-(β-hydroxyethyl)-3,4-dihydroisoquinolinium bromide (II), m. 157°, which was alkalized with aq. NaOH to give quant. 1-oxa-7,8-benzodidehydroindolizidine (III), $b_{0.02}$ 84–7°, m. 50°, also prepd. by treating I with ethylene oxide in MeOH 2 days. III with HBr gave II. To 80 g. $(CH_2)_4.CH{:}CCH_2CH_2NH_2$ (IV) with cooling and stirring was added dropwise 60 g. AcOH, the salt heated 2 hrs. under reflux, 2 hrs. with no condenser at 160–80°, 30 min. *in vacuo* at 120° to remove H_2O, and then distd. to give 89% the Ac deriv. (V), m. 53°. V (70 g.) in 350 ml. C_6H_6 refluxed 3 hrs. with 75 g. $POCl_3$ gave 42% 1-methyl-5,6,7,8-tetrahydroisoquinoline [b_{12} 114–16°; HCl salt m. 233° (decompn.); HBr salt m. 231°], and 35% 1-methyl-1,2,3,4,5,6,7,8-octahydroisoquinoline, b_{12} 101–2° (*N-p*-nitrobenzoyl deriv. m. 101°; 9,10-dibromide HBr salt m. 145–7° (decompn.); NAc deriv. b_{12} 158°. The *N*-formyl deriv. of IV failed to cyclize with $POCl_3$ to hexahydroisoquinoline. Norman Hosansky

CAOLD Reference #1

Synthesis and halomethylation of bis(3,4-dimethoxyphenyl) ether. Reaction of halomethyl derivatives with secondary amines and pyridines. Elisabeth Matarasso-Tchiroukhine (Sorbonne, Paris). *Compt. rend.* 250, 1867–9 (1960).—$[3,4\text{-}(MeO)_2C_6H_3]_2O$ (I) was prepd. by refluxing $3,4\text{-}(MeO)_2C_6H_3OK$, $3,4\text{-}(MeO)_2C_6H_3I$, and Cu powder in $HCONMe_2$ 18 hrs. Ether extn. of the dild., acidified mixt. and removal of the ether gave I, m. 94.5–95°. Treatment of I with MeCl in glacial HOAc gave $[2,4,5\text{-}Cl(MeO)_2C_6H_2]_2O$ (II), m. 121–22°. I, MeCl, HI, and Ac_2O gave the 2-ICH_2 analog (III) of II, m. 152°. The following derivs. of II and III were prepd.: pyridinium salts of II and III, m.p. not given and m. 172–3° (decompn.) (MeOH), resp.; isoquinolinium salts of II and III, m. 188–9° (decompn.) (MeOH–$HCONMe_2$) and m. 203–5° (decompn.) (MeOH), resp.; 2-morpholinomethyl analog of II, m. 216–17° (EtOH); and the 2-(Et_2NCH_2) analog of II, m. 142–4° (EtOH). John W. Hylin

The synthesis of esters of some amino acids having pharmacological importance. I. The synthesis of esters of piperidino carboxylic acids. Béla Matkovics, Sándor Foldeak, János Pórszász, and Gyorgy Sipos (Tudományegyetem, Szeged, Hung.). *Acta Pharm. Hung.* 31, 113–21 (1961)(in Hungarian).—RCH_2CO_2R' (I), $RCH_2CH_2CO_2R'$ (II), $BzOCH_2CH_2R$ (III), and $AcOCHMeCH_2R$ (IV) were prepd. I were prepd. by condensing $ClCH_2CO_2R'$ with a secondary amine, II by boiling $ClCH_2CH_2CO_2R'$ with the amine, and III by the reaction of an amino alc. with BzCl. The following I were obtained (R, R', b.p.°/mm., m.p. of picrate, m.p. of HCl salt, and m.p. of methiodide are given): piperidino, Me, 69°/5, 115°, 214°, 163–4°; piperidino, Et, 68°/1, 122°, 117–17.5°, 160–60.3°; piperidino, Bu, 100–1°/4, 85°, —, 178°; piperidino, $PhCH_2$, 134–5°/1, 137°, 133°, 91–6°; morpholino, Me, 77°/2, 143°, 150.5°, 147.5°; morpholino, Et, 86–7°/4, 163°, 181°, 132–3°; morpholino, Bu, 105.5–106°/3, —, 127–9°, 95–6°; morpholino, $PhCH_2$, 164–5°/5, 143°, 149°, —; pyrrolidino, Me, 72–3°/8, 104°, —, 153°; pyrrolidino, Et, 59–60°/2, 119.5°, 133–3.5°, —; pyrrolidino, Bu, 81–2°/3, 109.5°, —, —; pyrrolidino, $PhCH_2$, 134–5°/1, 159–60°, 139–40°, 156°. The following II were prepd. (data as above): piperidino, Me, 72°/2, 164°, 189°, 147–8°; piperidino, Et, 102–3°/5, 131.5°, 169°, —; piperidino, Bu, 124–5°/6, 108–9°, 164.7°, —; piperidino, $PhCH_2$, 149–50°/1, 113°, 193.5°, —; piperidino, Ph, 114–20°/3, —, 192–5°, —; piperidino, CPh_3, 171°/1, —, 214°, —; morpholino, Me, 82°/2, 129°, 203°, 151°; morpholino, Et, 108°/6, 108°, 188–9°, —; morpholino, Bu, 131–2°/6, 150°, 173°, 115°; morpholino, $PhCH_2$, 154°/1, 125°, 189–90°, —; pyrrolidino, Me, 76°/5, 147°, 128°, 166°; pyrrolidino, Et, 85°/6, 114°, 146°, —; pyrrolidino, Bu, 106–8°/5, 97°, 74–5°, 115°; pyrrolidino, $PhCH_2$, 145–6°/3, 102°, 152°, 154°. IV (R = pyrrolidino) (V), b_2 75°, picrate m. 111–12°, gave a hygroscopic HCl salt. III (R = piperidino) b_2 141°; HCl salt m. 184°; methiodide m. 141.5°. The action of the compds. on blood pressure and on respiration was given. II (R = N-piperidino, R' = CPh_3) and V had strong antinicotinic action. The effect of the piperidino and pyrrolidino propionates was increased by quaternization. E. Kasztreiner

Molecular structure of cyclic compounds containing sulfur. Kenjiro Hayasaki (Tokyo Gakugei Univ.). *J. Sci. Hiroshima Univ.* Ser. A 24, 679–90(1960).—Dipole moments of tri(thiobenzaldehyde) (I) (Baumann and Fromm, *Ber.*, 24, 1436(1891)), tri(thio-*p*-bromo- (II), and -*p*-chlorobenzaldehyde) (III) were detd. The values were used to investigate the structures and isomerism of trithiane rings. Infrared and Raman spectra of 1,4-dithiane (IV) were measured, and the structure of this ring system discussed. The skeletal frequencies of IV were calcd. by Wilson's method, assuming the Urey-Bradley-Shimanouchi field. III was prepd. by the Wörner method (*Ber.* 29, 154(1896)); α-isomer m. 162°, β-isomer 195.5°. Dipole moments reported were (compd., moment for α- and β-isomer given in D.): I, 2.09, 2.08; II, 2.17, 3.70; III, 2.21, 3.67. The α-isomers of I–III were assigned the chair (*a,e,e*) configuration and the β-isomers the chair (*e,e,e*) configuration. IV also had a chair configuration. H. H. Jaffé

Preparation and polymerization of *S,S'*-divinyldithiocarbonate. Helmut Ringsdorf and C. G. Overberger (Polytech. Inst. of Brooklyn, Brooklyn, N.Y.). *Makromol. Chem.* 44–46, 418–26(1961).—The title compd. (I) in benzene with free radical initiation gave a sol. polymer contg. the structural unit $SC(O)SCH(CH_2—)CH_2CH—$ and some residual unsatn. A soln. of 20 g. ethylene sulfide (II), 51 g. $COCl_2$ (III), and 3 drops pyridine was stirred 2 hrs. at −10 to −5°, then kept 10 hrs. at 25°, the excess III removed in a stream of N, and the residue distd. to give 65% $ClCOSCH_2CH_2Cl$ (IV), b_5 57.5°, a strong lacrimator and vesicant. A mixt. of 15.9 g. IV in 100 cc. $CHCl_3$ and 31.2 g. $BrCH_2CH_2NH_2.HBr$ vigorously stirred at 0° with 100 cc. 8% NaOH gave 91% $BrCH_2CH_2NHCOSCH_2CH_2Cl$, m. 89–90°. IV and PhSNa gave 93% $PhSCOSCH_2CH_2Cl$, $b_{0.2}$ 114–15°. II (60 g.), 49.5 g. III, and 3 drops pyridine kept at −5° and then 10 hrs. at 60° gave (on distn.) 12 g. IV and 76% $CO(SCH_2CH_2Cl)_2$ (V), $b_{0.1}$ 96–7°, m. 40–1°, a vesicant. V (60 g.) in 150 cc. anhyd. *tert*-BuOH was added dropwise to 60.5 g. *tert*-BuOK in 405 ml. *tert*-BuOH while the mixt. warmed to 50°. The mixt. was boiled 3 hrs., neutralized with HOAc, filtered, and distd. Redistn. of the fraction $b_{0.04}$ 60–80° gave 11% I, $b_{0.04}$ 73–4°. Other products of this reaction were $(tert\text{-}BuO)_2CO$, $CH_2{:}CHSCO_2Bu\text{-}tert$, and II. Polymerization of I was initiated by $(NCCMe_2N{:})_2$ (VI). In bulk, conversion of 20% or more gave insol. polymers swelled by C_6H_6, $CHCl_3$, and $HCONMe_2$. C_6H_6 solns. contg. approx. 1–30% I and 0.7–1.5% VI (calcd. on I) were polymerized at 60° under N with 11.5–60.9% conversion. The polymers were filtered, and pptd. from $CHCl_3$ soln. by MeOH. They softened at 300–10° with discoloration from 280° and rapid decompn. above 310°. The infrared spectrum showed only very weak absorption at 1590 $cm.^{-1}$ (vinyl group). Hydrolysis with KOH–MeOH under N gave a $(CH_2CHSH)_n$ sol. in dil. NaOH, cross-linked by traces of O. Otto S. Kauder

Condensation of ethyl nitroacetate with *o*-aminophenyl mercaptan. A. I. Kiprianov and T. M. Verbovskaya (Inst. Org. Chem., Kiev). *Zhur. Obshchei Khim.* 31, 531–7 (1961); cf. *CA* 50, 9387*c*; Mills, *CA* 16, 1954.—Heating *o*-$H_2NC_6H_4SH$ with $O_2NCH_2CO_2Et$ 4 hrs. at 100° gave 74% 2,3-dioxodihydrobenzo-1,4-thiazine 2-oxime, decompd. at 267°, also formed from $HONH_2$ and 2,2-dichloro-3-oxodihydrobenzo-1,4-thiazine (I) in EtOH in 79% yield; the oxime formed a mono-K salt, yellow, decompd. at 270°. The latter heated in xylene with Me_2SO_4 6 hrs. gave 79% Me ether (II), m. 251°, also formed from I and $MeONH_2$ in EtOH. The oxime refluxed with Ac_2O 2 hrs. gave the monoacetate, decompd. at 218°; BzCl in pyridine similarly gave monobenzoate, decompd. at 235°. Heating *o*-$MeNHC_6H_4SH$ with $O_2NCH_2CO_2Et$ 2 hrs. at 100° gave 54% 2,3-

2,4- and 3,5-$Et_2C_6H_3OH$. *o-EtC_6H_4OH* $b_{766.7}$ 202–3°, d_{20} 1.0177, n_D^{20} 1.5363; *p-isomer* $b_{766.7}$ 214–15°, 1.0097, 1.5328; *2,4-$Et_2C_6H_3OH$* $b_{766.7}$ 229–30°, 0.9811, 1.5264; *3,5-isomer* $b_{766.7}$ 242.5–5°, m. 76–6.5°. The neutral oil contains EtOPh and EtC_6H_4OEt. G. M. Kosolapoff

Synthesis of 2,6-diisopropylphenol. Shigeru Tsutsumi, Tadashi Yoshizawa, and Kikuhiko Koyama (Osaka Univ.). *Nippon Kagaku Zasshi* **77**, 737–8(1956).—In *C.A.* 52, 304*b*, lines 8 and 9, the compd. should be 2-isopropyl-4-chlorophenol, b_7 121–26°, and I should be 2,6-diisopropyl-4-chlorophenol. R. E. S.

Triphenyloxonium salts. A. N. Nesmeyanov and T. P. Tolstaya (M. V. Lomonosov State Univ., Moscow). *Doklady Akad. Nauk S.S.S.R.* **117**, 626–8(1957).—Ph_2O (150 g.) treated at 80–90° with 10.5 g. PhN_2BF_4 in 300 ml. Me_2CO, heated 0.5 hr., cooled, washed with 50% Me_2CO, the filtrate extd. with Et_2O, and the ext. evapd. gave 2% *Ph_3OBF_4*, decomp. 226° (Et_2O-Me_2CO). Also prepd. were: 63% *Ph_3OCl*, decomp. 193–4°; 72% *Ph_3OBr*, decomp. 182–2.5°; *Ph_3OI*, decomp. 177–8°; *Ph_3OHgI_3*, decomp. 156–7°; *Ph_3OBPh_4*, decomp. about 165°; *Ph_3OPtCl_6*, decomp. 184–5°; *Ph_3OCr_2O*, decomp. 180°; *Ph_3OICl_4*, decomp. 167–71°; *Ph_3O picrate*, decomp. 155–7°. Refluxing Ph_3OBF_4 25 hrs. in H_2O left some 50% unchanged. Such refluxing with aq. $NaNO_2$ gave some 25% $PhNO_2$ isolated after reduction to $PhNH_2$. Refluxing Ph_3OBF_4 with aq. NaN_3 14.5 hrs. gave 27% PhN_3, isolated after reduction to $PhNH_2$. Ph_3OBF_4 refluxed 8.5 hrs. with aq. Et_2NH gave 59% $PhNEt_2$, isolated by azo coupling with nitraniline. Refluxing Ph_3OBF_4 in pyridine 4 hrs. gave 1-phenylpyridinium fluoborate, 89%, m. 177.5–8.5°. Absorption spectra of the Ph_3O salts are reproduced. G. M. Kosolapoff

Preparation and transformation of *p*-diethylbenzene hydroperoxide. P. G. Sergeev and A. M. Sladkov. *Zhur. Obshchei Khim.* **27**, 3349–53(1957).—Reduction of *p*-AcC_6H_4Et with 80% $N_2H_4.H_2O$ and KOH in $O(CH_2CH_2OH)_2$ at 260° gave about 20% *p*-$C_6H_4Et_2$, b_{14} 70°, d_{20} 0.860, n_D^{20} 1.4947. This percolated with air at 110° in the presence of $Ni(OBz)_2$ 15–18 hrs. gave after treatment with aq. NaOH and extn. with Et_2O followed by percolation of the alk. soln. with CO_2 and extn. with Et_2O an unstated yield (about 16%) of *p-diethylbenzene hydroperoxide*, n_D^{24} 1.5231, 94.2% assay. This heated in Me_3CPh 3 hrs. at 130° gave 75% *p*-AcC_6H_4Et. Reduction of the hydroperoxide with $LiAlH_4$ gave 70% *p*-$EtC_6H_4CHMeOH$, b_{15} 121–2°. Stirring the hydroperoxide in C_6H_6 with 1 drop H_2SO_4 1 hr. gave C_6H_6, *p*-EtC_6H_4OH, and AcH. G. M. Kosolapoff

The rearrangement of benzenesulfonyl chloride with sodium iodide in acetone. H. Kroepelin and K. Born (Tech. Hochschule, Braunschweig, Ger.). *Arch. Pharm.* **287**, 561–5(1954); cf. *C.A.* 21, 573.—Treating 15 g. $PhSO_2Cl$ with 26 g. NaI in 200 ml. Me_2CO gives after 2½ hrs. and subsequent processing 60.3% Na benzenesulfinate, 27.8% diphenyl disulfone, m. 191–2°, and 10.5% Ph phenylthiosulfinate, m. 41–2°. The reaction mechanism is discussed. Henry B. Hastie

Some new phenethylamines. J. R. Merchant and A. J. Mountvala (Inst. Sci., Bombay). *Current Sci.* (India) **26**, 211–12(1957).—A series of phenethylamines was prepd. by the reaction of an aldehyde and $MeNO_2$ in the presence of AcOH and NH_4OAc to give a β-nitrostyrene which was then reduced with $LiAlH_4$. The following substituted phenethylamines were isolated as their picrates (substituents and m.p. given): 2,4,6-$(MeO)_2Me$, 117°; 2,4,6-$(EtO)_2Me$, 115°; 2,4,6-(EtO)(MeO)Me, 135°; 2,6,4-Me_2(MeO), 115°; 2,6,4-Me_2(EtO), 81°; 2,4,6-Me_2(MeO), 140°; 2,4,6-Me_2(EtO), 113°; 2,3-$PhCH_2O$(MeO), — (oil); and 2,3,5-(MeO_3), 102°. P. Melius

New method of syntheses of musk ambrette. Hiroshi Horiguchi (Kobe Univ.). *Koryo* No. 47, 18–39(1957).—Musk ambrette (I) was synthesized from *o*-nitrotoluene. Thus, *o*-nitrotoluene was reduced to *o*-tolylhydroxylamine (II) with Zn powder in MeOH. When II was heated in MeOH with concd. H_2SO_4, II was rearranged to amino-*m*-cresol Me ether (III). *m*-Cresol Me ether (IV) was prepd. by a deamination of diazotized III. The yield of IV was 45% from *o*-nitrotoluene. I was prepd. from IV as usual. S. Inokawa

Synthesis of guanidine compounds of diphenyl ether. I. Genzo Ito (Pharm. Hochschule Meiji, Tokyo). *Pharm. Bull.* (Tokyo) **5**, 397–400(1957)(in German).—To find new compds. active against tuberculosis, there were synthesized 8 derivs. of $PhOC_6H_4NHC(:NH)NH_2$ (I) and 3 derivs. of $PhOC_6H_4CH_2NHC(:NH)NH_2$ (II). The HCl salt of 4-$H_2NC_6H_4OPh$ (III) (5.5 g.) and 1.6 g. H_2NCN refluxed 3 hrs. in 35 cc. abs. EtOH, the solvent removed, and the sirupy residue dissolved in H_2O and made alk. with NaOH yielded 5.9 g. I (guanidino group in 4-position), m. 137° (C_6H_6); nitrate, m. 173°; picrate, m. 205°. Similarly from 2- and 3-H_2N derivs. of Ph_2O were synthesized I (guanidino group in 2- and 3-positions), nitrates, m. 139° and 173°, resp.; and from the 4′-Me, 4′-Cl, 4′-Br, and 4′-guanidino derivs. of III, the corresponding derivs. of I, nitrates, m. 162°, 186°, 189°, and 223°, resp. The 4′-HO deriv. of I was prepd. in 3 steps: adding 2.5 g. 4,4′-O_2N(MeO) deriv. (IV) of Ph_2O to 2.7 g. dry $AlCl_3$ in 20 cc. warm $PhNO_2$, heating the mixt. 2 hrs. at 50–5°, pouring it gradually into H_2O contg. 10 cc. concd. HCl and ice, steam-distg. the org. layer to remove $PhNO_2$, and extg. the residue with hot 5% NaOH yielded from the ext. 1 g. solid unchanged IV, and from the acidified filtrate 1 g. 4,4′-O_2N(HO) deriv. (V) of Ph_2O, m. 172° (C_6H_6). V (2.3 g.) reduced in 20 cc. abs. EtOH with 3 g. $N_2H_4.H_2O$ and a little Raney Ni (Balcom and Furst, *C.A.* 49, 8158*d*) yielded 1.8 g. of the corresponding 4,4′-H_2N(HO) deriv., m. 152° (C_6H_6), and this treated as III was with H_2NCN gave the 4′-HO deriv. of I, m. 223°; HCl salt, m. 242°; flavianate, m. 200°. For the prepn. of II, 92 g. 4-MeC_6H_4OPh in 200 g. $(CH_2Br)_2$ gently boiling on an oil bath was treated dropwise in sunlight with 80 g. Br in 50 g. $(CH_2Br)_2$ with stirring during 1 hr., stirred an addnl. 1 hr., and the cooled mixt. neutralized with solid K_2CO_3 and distd. *in vacuo* to yield 97 g. 4-$BrCH_2C_6H_4OPh$ (VI), b_6 157–60°. 2-$BrCH_2C_6H_4OPh$, b_8 135–40°, was similarly prepd. Dry HCl passed through 68 g. VI, 38 g. $(CH_2)_6N_4$, and 42 g. NaI in 350 cc. 95% EtOH pptd. NH_4Cl, and the filtrate evapd. yielded 25 g. HCl salt of 4-$H_2NCH_2C_6H_4OPh$ (VII), which in concd. aq. soln. made alk. and extd. with $CHCl_3$ gave an oil; nitrate, m. 170° (decompn.) (H_2O); benzoate, m. 127° (MeOH). 2-$H_2NCH_2C_6H_4OPh$ (VIII), nitrate, m. 153° (decompn.) (H_2O), was similarly prepd. Similarly, from 26.4 g. 4′-O_2N deriv. of the Cl analog of VI (Southwick, *et al.*, *C.A.* 49, 955*e*) was prepd. 10 g. HCl salt of the 4′-O_2N deriv. of VII; the free base an orange-yellow viscous oil; Ac deriv. (IX), m. 120°. IX (28.6 g.) reduced as V was yielded 21 g. 4-$AcNHCH_2C_6H_4OC_6H_4NH_2$-4′ (X), m. 146°. X (12.8 g.) diazotized in the usual way, the mixt. refluxed 3 hrs. with 2 g. urea, and worked up as usual yielded 3.1 g. 4′-HO deriv. (XI) of VII, m. 182° (EtOH); picrolonate, m. 230–2° (decompn.) (MeOH-AcOEt). VII (2 g.) in 30 cc. abs. EtOH refluxed 3 hrs. with 2.6 g. $MeSC(:NH)NH_2.HI$ (XII), EtOH distd. off, and the residue in a little H_2O treated with NH_4NO_3 gave the nitrate of II, m. 157° (Me_2CO-AcOEt). Similar treatment of VIII gave the nitrate of its corresponding guanidino compd., m. 132°. XI (1.8 g.) in 20 cc. abs. EtOH refluxed 2 hrs. with 2.2 g. XII yielded on evapn. of EtOH 2.4 g. 4′-HO deriv. of II; HI salt, m. 227° (decompn.); picrolonate, m. 265–70° (decompn.) (EtOH). All 11 guanidino derivs. gave a pos. Sakaguchi reaction, a violet-red color with 2-naphthol and NaOBr. The effect of these 11 compds. against tuberculosis bacilli *in vitro* was detd. according to Tomita and Watanabe (*C.A.* 46, 7617*h*), and none was very effective. **II. A new synthesis of diphenyl ether aldehyde by the Sommelet reaction and experiments with methylguanidine derivatives.** 1. *Ibid.* 401–5.—Four compds. similar to the preceding but contg. 2 CH_2 groups between the guanidino group and the Ph_2O nucleus were prepd. According to the Sommelet reaction 66 g. 4-$BrCH_2C_6H_4OPh$ (I) and 38.5 g. $(CH_2)_6N_4$ in 200 cc. $CHCl_3$ were refluxed 4 hrs., and cooled to yield 85 g. of the condensation product, which (101 g.) with 35 g. addnl. $(CH_2)_6N_4$ was hydrolyzed by refluxing 2 hrs. with 400 cc. 50% AcOH, an addnl. 10 min. with 100 cc. concd. HCl, cooling, and extg. with ether to yield 33.5 g. 4-$OHCC_6H_4OPh$ (II), b_6 157–60°; phenylhydrazone, m. 144°; semicarbazone, m. 214–15°. 2-$OHCC_6H_4OPh$ (III) was similarly prepd., b_8 156–9°; semicarbazone, m. 207–8°. Bromination of 107 g. 4′-MeO deriv. of 4-MeC_6H_4OPh with Br in $(CH_2Br)_2$ (preceding abstr.) yielded the 4′-MeO deriv. of I, which without isolation underwent the Sommelet reaction (like I above) to yield 51 g. 4′-MeO deriv. (IV) of II, m. 57–9° (petr. ether); semicarbazone, m. 212°. Reaction with $MeNO_2$ changed the CHO group of II, III, and IV to $O_2NCH:CH$ (IIa, IIIa, and IVa): IIa, m. 100°, 21 g. from 30 g. II; IIIa, m. 107°; IVa, m. 77°, 11.3 g. from 38 g. IV. IIa, IIIa, and IVa were reduced by $LiAlH_4$ in the usual way to the corresponding $H_2NCH_2CH_2$ derivs. (IIb, IIIb, IVb):

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